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PIEZOELECTRIC AND PYROELECTRIC APPLICATIONS OF PLASTICS

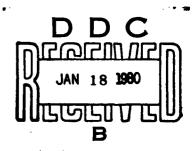
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Prepared for Symposium

American Chemical Society
Organic Coatings and Plastics Chemistry Division

National Bureau of Standards Polymer Science & Standards Division Washington, D.C. 20234



January 1980

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National Bureau of Standards PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS Polymer Science & Standards Division Task No. 12139 Washington, D.C. 20234 11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research REPORT DATE Jane Chemistry Program THEER OF PAGE Arlington, VA 22217 15. SECURITY CLASS. (of this report) 14. MONITORING AGENCY NAME & ADDRESS(II Unclassified 154. DECLASSIFICATION/DOWNGRADING 16. DISTRIBUTION STATEMENT (of this Report) DISTRIBUTION STATEMENT A Approved for public releases Distribution Unlimited 17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) Submitted to Symposium on New Applications for Plastics, American Chemical Society, Organic Coatings and Plastics Chemistry Division, Houston, Texas March 23-28, 1980. 19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Applications; piezoelectric; polymers; pyroelectric; transducers. TRACT (Continue on reverse side if necessary and identify by block number) This paper summarizes the advantages and disadvantages of polymer piezoelectric and pyroelectric transducers relative to transducers made of ceramic materials. It is concluded that polymers are the material of choice for some special measurement problems and inferior for others. A large list of applications ranging from commercial to exploratory is given with references to further information.

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PIEZOELECTRIC AND PYROELECTRIC APPLICATIONS OF PLASTICS

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Synthetic polymeric materials can have large and durable electric dipole polarization. This polarization varies linearly with small applied stresses such as electric fields, mechanical stress and temperature change, and this sensitivity renders them useful as piezoelectric and pyroelectric transducers. That is, they can be used to provide an analog electrical signal to monitor mechanical and thermal signals, and inversely, can provide mechanical motion and changes in heat content in response to applied electric fields.

Polymers, only recently (since 1969) recognized as potentially important transducer materials, have several advantages over more conventional ceramic transducer materials. Ceramics are hard, stiff, brittle, heavy, difficult to produce in large sizes and to machine into complex shapes. Polymers are soft, pliable, tough, light weight and easily fabricated into large sheets and cut or bent into complex shapes and they are inexpensive to produce. Ceramic materials are usually mounted in housings with metal bases and require relatively large-area flat surfaces and hardware for mounting. The polymer can simply be glued to small non-flat surfaces by means of rubber cement, cyanoacrylate, epoxy or other cement. A ceramic transducer is subject to damage from mechanical shock or twisting and bending stresses, whereas a polymer has a much higher tolerance for severe mechanical strain. Ceramics usually have higher dielectric constants than polymers. This increases the capacitance of a transducer and reduces the voltage response arising from the charge produced by a given pressure or temperature change. Often the polymer is used as a thin film which also leads to high capacitance. Ceramics are relatively high Q materials with large resonances. Polymers are mechanically "lossy" with much flatter response over a wide range of frequencies. Because of their light weight, polymers have a smaller perturbing effect on the motions of structures to which they are attached. The low mechanical impedance of polymers provides a good mechanical match to liquids and biological tissue so that when used with these "soft" materials more complete energy transfer occurs into the transducer and there are fewer reflections and distortions of the wave pattern at the transducer interfaces. The availability of large sheets of polymer greatly facilitates fatrication of transducer arrays, which are used for electromagnetic or acoustical imaging.

The main disadvantages of polymer transducers are their relatively low piezoelectric and pyroelectric output and relatively poor dimensional stability. A comparison of typical values of activity is shown in Table I. The piezoelectric voltage response of the polymers is quite good when compared to ceramics of the same thickness. However, the polymers are not easily available in larger thicknesses common to ceramics, so that the polymers are typically less sensitive than ceramics. The poor dimensional stabilities of polymers are due in part to mechanical relaxation of residual stresses, and leads to relaxation of transducer polarization. The longer the time scale for a pressure or temperature change being measured the greater will be the measurement uncertainty due to electrical drifts arising from sample relaxation. For static measurements requiring high accuracy, a provision may be required for periodic calibration of the polymer transducer. The melting or softening points of polymers are lower than those of ceramics and the prolonged use of polymers is presently limited to below about 100°C.

Two types of polymers are useful as transducer material--semicrystalline and amorphous. Semicrystalline polymers like polyvinylidene fluoride (PVDF) and polyvinyl fluoride (PVF) have electrically polar crystal phases where the polarity can be reoriented with large electric fields applied even below room temperature. The amorphous phase acts merely to couple the crystals together. These polymers are much like the composites of piezoelectric ceramic powders dispersed in a rubbery matrix which are sometimes used as transducer material, except that the polymer crystals are less dense and more tightly interconnected. These semicrystalline polymers are ferroelectric and can be oriented to achieve about half of their theoretical maximum polarization. Attempts to find a piezoelectric polymer better than PVDF have yet to be successful.

Amorphous polymers like polyvinyl chloride (PVC) and poly acrylonitrile (PAN) are not ferroelectric. Their polarization is due to a distribution of dipole orientations typical of a polar liquid in equilibrium with a large applied electric field. Because this polarization rarely exceeds a few percent of that for complete alignment of dipoles, these amorphous polymers are typically an order of magnitude less active than semicrystalline polymers and the practical temperature range for prolonged use extends only up to about 50°C, i.e. their glass transition temperatures. However, since the polarization process in amorphous polymers is more straightforward than in semicrystalline polymers it is easier to engineer a material with high polarity and high glass transition temperature which would be useful for high temperature transducers. The possibility of stabilizing polarization by chemical cross links is promising but has received very little attention.

Numerous applications for piezoelectric and pyroelectric polymers have been explored and some have been commercialized. Table II lists a variety of such applications and gives references to be used for further information. At the National Bureau of Standards, several applications have been found to aid government agencies with unique transducer measurement problems. For example, cooperative work with the Bureau of Radiological Health has yielded a miniature hydrophone having a 1 mm diameter sensor which can be used for precision calibration of the sound fields from a therapeutic or diagnostic ultrasonic acoustic device. The hydrophone gives negligible distortion of the sound field being measured. Such detailed calibration is needed to avoid damaging patients with excessive levels of ultrasound while at the same time providing the maximum safe intensity. Cooperative work with the Bureau of Engraving and Printing has yielded a transducer to measure the nip pressure of presses used in printing currency and stamps (the nip is the region of contact between the printing plate and upper cylinder). Measurement of this pressure has proven an elusive problem and is important not only to monitor and control printing pressures but also to provide data for the improvement of ink and other printing materials.

The growth in polymer transducer applications has been gradual over the past 10 years. This is largely because polymer transducer performance is not so outstanding that polymers will replace ceramic transducers in all applications. However, the unique properties of polymers make them suitable for a large variety of measurement problems which are now being identified and developed and the future of polymers in transducer applications seems assured.

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Table I

COMPARISON OF POLYMERIC AND NON-POLYMERIC SUBSTANCES

Substance	. d		$g = d/\epsilon_0 \epsilon'$	р	p/ε ₀ ε'
	(10 ⁻¹² m/V	or C/N)	$(10^{-3} \text{V} \cdot \text{m/N})$	$(10^{-9} \text{ C/cm} \cdot \text{K})$	
Quartz	2	đ	50		
Barium Titanate	190	đ	12	20 📽	1.3
Triglycine Sulfate	-		•	30 *	100
Poly(vinylidene fluoride	e) 30	đ	350	3	34
Poly(vinyl chloride)	1.	5 ^{<i>b</i>}	65	0.3 ^{<i>b</i>}	11
Mahari 11 0-6 3 - 41 0-6				•	

Notes: b) Ref.1, d) Ref.2, e) Ref.3

Table II

APPLICATIONS OF PIEZOELECTRIC AND PYROELECTRIC POLYMERS

Application	Reference for Further Information
Audio Speakers	4-6
Headphones	4
Microphones	7
Telephone	7,8
Finger pressure sensor switch	9
-for telephones	. 10,11
-for typewriters	12
Hydrophones	9,13-16
Impact detector	17
Stress wave Monitor	17
-in rock	18
-in soil	19,20
Strain Guage	21
Pressure Sensor for Presses used for	
printing and paper and film making	22
Vibration damper	23
Anti Fouling Applications	24,25
Acoustic Retina	26
Bimorph for visual display	27 ,28
Pulse Monitor	5
Bone Healing Implant	. 29
Fuze and Detonator for Explosives	30
Bearing Wear Monitor	· 31
Acoustic Emission Sensor	18,32,33
Accelerometer	34
Cartridge for Disk Records	4
Heat Exchanger Membrane	35
Varia ble Focus Mirror	36
Optical Second Harmonic Generator	37
Ultrasonic Transducer for Light	
Moderation and Deflection	38
Infra Red Detector	9,39
Heat Scanner	40
Intrusion Detector	41,42
Photocopy Process	43
Absolute Reflectivity Detector	44
Radiometer	45
Vidicon Target	46
Laser-Beam-Profile Array	· •

REFERENCES

- 1. M. G. Broadhurst, W. P. Harris, F. I. Mopsik and C. G. Malmberg, Polymer Preprints (Papers presented at the American Chemical Society Meeting in Chicago, March, 1973):14, 820 (1973).
- 2. E. Fukada, <u>Electrets</u>, p.486, Edited by Martin M. Perlman (The Electrochemical Society, Princeton, NJ, 1973).
- 3. E. H. Putley, <u>Semiconductors and Semimetals</u>, Vol.5, p.259 (Academic Press, NY, 1970).
- 4. N. Tamura, T. Yamaguchi, T. Oyaba and T. Yoshimi, J. Audio Eng. Soc. 23, p.21 (1975).
- 5. S. Hunklinger, H. Sussner and K. Dransfeld, Advances in Solid State Physics, J. Treusch, Ed. Vieweg, Braunschweig XVI, p.267 (1976).
- 6. F. Micheron and C. Lemonom, J. Acoust. Soc. of America, 64, 1720 (1978).
- 7. J. F. Sear, Electron 94, 36 (1976).
- 8. The British Post Office and other telephone companies are investigating this application.
- 9. H. R. Gallantree and R. M. Quillian, The Marconi Review, Forth Quarter, 189 (1976).
- 10. N. Murayama, K. Nakamura, H. Obara and M. Segawa, Ultrasonics 14, 15 (1976).
- 11. G. T. Pearman, J. L. Hokanson and T. R. Meeker, Ferroelectrics (Special issue of papers presented at Symposium on Applications of Ferroelectrics, Minneapolis, June 1979) to be published.
- 12. H. Ohigashi, private communication.
- 13. J. M. Powers and T. D. Sullivan, J. Acoust. Soc. Am. 60 547, (1976).
- 14. S. Edelman. J. Acoust. Soc. Am. 48, 1040 (1970).
- 15. A. S. DeReggi, S. Roth, J. M. Kenney, S. Edelman and G. Harris, J. Acoust. Soc. Am. <u>64</u>, 555 (1978).
- 16. S. Edelman, Proc. Workshop on Sonar Transducer Materials, P. L. Smith and R. C. Pohonka, Eds., Naval Res. Lab. (1975).
- 17. A. S. DeReggi, S. Edelman and S. C. Roth, Natl. Bur. Stds. Interagency Report No. 76-1078 (1976).
- 18. B. T. Brady, Nature, <u>260</u>, 108 (1976).
- 19. S. Edelman, Tech. Report No. AFWL-TR-73-186, Air Force Weapons Lab (1973).
- 20. R. B. Bunker, Eighth Transducer Workshop, Telemetry Group, Range Commanders Council (1975).
- 21. S. Edelman, preliminary results.
- 22. S. Edelman, S. C. Roth, A. S. DeReggi and J. Kenney, 10th Annual Symposium on Paper and Pulp Technology, Miami U., Oxford, OH (1979).
- 23. S. Edelman, S. C. Roth and L. R. Grisham, The Shock and Vibration Bulletin, 39, 1 (1969).

- 24. M. Latour, O. Guelorget and P. V. Murphy, Extended Abstracts of the 1978 Int'l. Workshop on Electric Charges in Dielectrics, Kyoto, Japan (1978).
- 25. 8. Wooden and S. Edelman, patent disclosure (1975).
- 26. A. S. DeReggi, S. Edelman, S. Roth, H. Warner and J. Wynn, J. Acoust. Soc. Am., 61, 517 (1977).
- 27. M. Toda, Trans. Inst. of Electronic and Communications Engineers of Japan, <u>E6</u>1 5-7 (1978). Ibid, page 507.
- 28. M. Toda and S.Osaka, Proceedings of the SID 19 35, (1978).
- 29. E. Fukada, private communication.
- 30. P. E. Bloomfield, Nat'l. Bur. Stds Interagency Report No. 75-724(R) (1975).
- 31. S. Edelman, J. M. Kenney, J. F. Mayo-Wells, S. C. Roth, Proc. 28th Meeting Mechanical Failures Prevention Group, T. R. Shives and W. A. Willard, Eds. Nat'l. Bur. Stds. Symposium Proceedings No. 547 (1979).
- 32. W. M. McCabe, Proc. Second Conf. on Acoust. Emmission/Microseismic Activity on Geological Structures and Materials, Penn. State Univ. (1978).
- 33. W. R. Scott and J. Carlyle, Naval Development Center Report No.3930(1975).
- 34. S. Edelman, design developed.
- 35. S. Edelman and L. D. Ballard, patent disclosure (1978).
- **36.** S. A. Kokorowski, J. Opt. Soc. Am. <u>69</u>, 181 (1979).
- 37. J. H. McFee, J. G. Bergman, Jr. and G. R. Crane, Ferroelectrics, 3, 305 (1972). (Also in IEEE Trans. Sonics and Ultrasonics SV19, 305 (1972).)
- **38.** H. Ohigashi, R. Shigenari and M. Yokota, Japan J. Appl. Phys. <u>14</u>, 1085 (1975).
- 39. Nat'1. Bur. Stds. Interagency Report No. 75-728 (1975).
- 40. Developed and sold by 3-M Company
- 41. J. Stern and S. Edelman, Nat'l. Bur. of Stds. Technical News Bulletin 56, No. 3, 52 (1.72).
- 42. Some passive infrared sensitive detectors are being sold commercially.
- 43. J. G. Bergman, G. R. Crane, A. A. Ballman and H. M. O'Bryant, Jr. Appl. Phys. Lett. 21 497 (1972).
- 44. W. R. Blevin and J. Geist, Appl. Opt. 13, 2212 (1974).
- R. L. Peterson, G. W. Day, P. M. Gruzensky and R. J. Phelan, Jr. J. Appl. Phys. 45 3296 (1974). Also IR100 Award, Industrial Research 17, 46(1975).
- 46. L. E. Garn and E. J. Sharp, IEEE Trans, in Parts, Hybrids and Packaging, PHP10, 28 (1974).

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